A Theory of Surface Tension of Aqueous Solutions of Inorganic Acids.

By Kyozo ARIYAMA.

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1. Introduction. Since Heydweiller and his co-workers[1] discovered that the surface tension of the solution of inorganic salts in water increases as the solute is increased, various attempts[2] have been made to explain the phenomenon. The recent theories proposed[3],[4],[5],[6] to account for the phenomenon are all based on the Debye-Hückel[7] theory of strong electrolyte. All these theories treated with varied degrees of success the normal effect, that is, the increase of surface tension with increase in the concentration of the electrolyte. None of these theories, however, treat the anomalous behaviour of inorganic acids which exhibit a decrease of surface tension as the concentration is increased. The lack of any theoretical account for the anomalous effect for inorganic acids is due primarily to the fact that the effect is just opposite to what we might expect from the Debye-Hückel theory of strong electrolyte. This simple fact suggests at once that the structure of water at the surface is the most important factor to be considered in any theoretical discussion of this anomaly. The present paper shows that the anomaly can be explained quantitatively if we accept two hypotheses, that is, a special orientation of water molecules at the surface different from the interior and the semi-empirical structure of water as proposed by Bernard and Fowler.[8]

2. In order to understand the especially high value found for the decrease of surface tension due to ammonia solution of water, we shall discuss briefly the structure of water and similar compounds from a general point of view.[9]

The hydrogen atom occupies a very peculiar position in the structure of atoms, and exhibits in many ways peculiar characteristics different

(1) Heydweiller, *Ann. Physik*, [4], **33** (1910), 145.
(2) Wagner, *Physik. Z.*, **25** (1924), 474.
(3) Onsager and Samaras, *J. Chem. Phys.*, **2** (1934), 529.
(4) Oka, *Proc. Phys.-Math. Soc. Japan*, [3], **14** (1932), 649.
(5) Shiba, *Bull. Inst. Phys. Chem. Research* (Tokyo), **8** (1934), 110.
(6) Ariyama, this Bulletin, **11** (1936), 887.
(7) See for example Falkenhagen, "Electrolyte."
(8) Bernal and Fowler, *J. Chem. Phys.*, **1** (1933), 515.
(9) The author is indebted to Dr. J. Horiuchi for the following discussion.

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from all other elements. Most of these peculiarities owe their origin to the fact that the positive ion of the hydrogen atom is simply a proton, which carries no extra-nuclear electrons. An example of such peculiarity is given in the case of an extraordinarily high absorption of hydrogen by palladium. This is explained if we consider that the hydrogen atom when going into palladium separates into electron and proton, and that these are separately absorbed.[10] The greatest peculiarities appear when hydrogen atoms combine with atoms of oxygen or nitrogen.

The peculiarities are indicated in the structure of the compounds as well as in various chemical and physical properties of the compounds. In the case of water, for example, the distance between the two hydrogen atoms is 0.97Å, while the diameter of hydrogen molecule is 2.76Å. Thus two protons of the water molecule lie within the distance of orbital radius of the outermost electrons of oxygen atoms. Bernal and Fowler[8] in their extensive treatment on water give the following model for the structure of water, basing their argument partially on quantum mechanics and partially on experimental data: If we suppose an oxygen atom at the center of a tetrahedron the two heads of the tetrahedron are occupied by the two protons, and at the other two heads of the tetrahedron are distributed the negative charges. The structure of alcohol is obtained if we replace a hydrogen with an alkyl radical in the tetrahedron. In the case of ammonia, three corners of the tetrahedron are occupied by protons and the remaining corner is occupied by negative charges. If we replace one hydrogen by alkyl radicals we obtain the structure for amines.

If, for example, molecules which have similar structure to water approach a water molecule, it is quite evident from the above discussion that the corners of the tetrahedron of water at which negative charges are distributed will attract the protons of other molecules. Such union of two molecules by means of a proton is called a "hydrogen bond," and this hydrogen bond is considered responsible for the association of water, alcohol, and ammonia molecules.

From these general discussions it may be expected that the hydrogen ions and ammonia molecules behave somewhat differently from all other inorganic ions in water. If the molecules of water are distributed at random both at the surface and in the interior of the liquid, the negative adsorption should result from solutions of inorganic acid. For the ions forming the hydrogen bond between molecules of water will be uniformly distributed everywhere so that the effect due to hydrogen bond can be neglected as far as the distribution of hydrogen ions in water is concerned.

(10) Frank, *Göttinger Nachrichten*, **1933**, 293.

Thus the hydrogen bond alone does not give rise to the positive adsorption of hydrogen ions at the surface of water.

In order that the positive adsorption of hydrogen ions at the surface of water should result the distribution of the hydrogen bond must be different at the surface than in the interior of the water. If at the surface the number of water molecules having their hydrogen heads facing upward sufficiently exceeds the number having their oxygen atoms facing upward so that as a consequence there is a resultant of hydrogen heads extending into the liquid, we might expect positive adsorption of hydrogen ions at the surface due to the hydrogen bond. Since this seems to be the only way for the positive adsorption of hydrogen ions to occur at the surface, we shall assume that the majority of water molecules are oriented at the surface in such a way that the proton heads of the molecular tetrahedrons lie on the surface causing the negatively charged corners to extend downward into the liquid.

3. For the quantitative discussion of the surface tension of inorganic acids, we shall take, for sake of simplicity and convenience, one-half molar concentration for all the compounds, and the temperature at which the surface tension is given is corrected to 20°C. unless otherwise stated. The Table 1 shows the experimental data mainly collected from the International Critical Tables.

In the fourth row of the Table the calculated values for the surface tension decrease due to one hydrogen-bond at the surface are given. The methods of the calculations are given in the following: We shall take the case of HCl as an example. The surface tension increase due to half normal solution of NaCl at 20° is 0.83 dynes/cm. Since the charge of Na^+ and Cl^- ions are the same, and their ionic volume approximately the same according to the theories proposed for the negative adsorption of Debye-Hückel electrolyte,[3],[4],[5],[6] the contribution of these two ions to the increase of the surface tension of the solution will be approximately the same. Thus we get the same contribution from Na^+ as from Cl^- namely 0.41 dynes/cm. If the Cl^- behaves in the same way in the half normal solution of HCl as in the half normal solution of NaCl, then the contribution of Cl^- to the increase in surface tension will be the same. Therefore, in order to obtain the decrease of the surface tension of the HCl solution by -0.2 dynes/cm., the contribution due to H^+ should be $-0.2 - 0.41 = -0.61$. dynes/cm. In the similar manner the contribution due to one hydrogen bond for the compounds HNO_3 and HBr is calculated. The values assigned for negative ions for respective compounds are listed

(11) Rice, *J. Phys. Chem.*, **32** (1928), 583.

Table 1.

$\Delta\gamma$ is the difference between the surface tension of the solution and that of the solvent at the same temperature.
$\Delta\gamma$ is expressed in dynes per centimeter.

Formula	Temperature °C.	$\Delta\gamma$ for 0.5 mol/kg.	$\Delta\gamma$ due to H
HCl	20	−0.16	−0.57±0.1
NH_3	18	−1.4	−0.46±0.3
HNO_3	20	−0.42	−0.61±0.2
HBr	18	−0.38±0.2	−0.56±0.2
H_2SO_4[12]	20	−0.18	−0.55±0.3
Na_2HPO_4	30	−0.81±0.2	−0.23±0.3
KH_2PO_4[12]	20	−0.53±0.05	−0.81±0.3
H_3PO_4[12]	20	0.00±0.3	−0.33±0.3
		The average for the last 3 cases	−0.46±0.3

Table 2.

Uni-valent case

Ions	$\Delta\gamma$
Na^+	0.41
Cl^-	0.41
NO_3^-	0.19
OH^-	0.50
Br^-	0.29
NH_4^+	0.5

Bi-valent case

Ions	$\Delta\gamma$
Na^+	0.23
SO_4^{--}	0.91

Tri-valent case

Na^+	0.11
K^+	0.11
PO_4^{---}	0.99

in the Table 2. These values can be used to check their reasonableness with many other compounds containing these negative ions in the solutions.

When the negative ions happen to be bi-valent or of the higher valency, the calculation is carried out in the following manner: Let us take as an example the half normal solution of Na_2SO_4. According to the theories of the negative adsorption,[3],[4],[5],[6] the contribution of ions

(12) Morgan and Bole, *J. Am. Chem. Soc.*, **35** (1913), 1750.

to the increase in the surface tension of the solution is proportional to the number of respective ions and to the squares of their ionic charges. Thus the increase of surface tension by 1.36 dynes/cm. for the Na_2SO_4 solution gives 0.91 dynes/cm. to SO_4 ions, that is 4/6 of the total effect. A similar argument applies to the case of H_3PO_4 and the related compounds. The values assigned for the negative ions are given in Table 2. Using these values for the negative ions, we obtain values for one hydrogen-bond for various compounds.

The calculation for ammonia differs from the above procedure. As we have already discussed, the ammonia molecule has a very similar structure to water, and any one of three protons of the ammonia molecule can form a hydrogen bond with a water molecule. Thus the probability of ammonia being adsorbed by water molecules at the surface is approximately three times as large as that of single hydrogen ion, so that it is to be expected that the half normal ammonia solution will show three times as large an effect as is to be expected from HCl solution. Therefore, we simply divide -1.4 dynes/cm. by 3 to obtain the effect due to a single hydrogen bond. We obtain a value for the single hydrogen-bond which agrees within experimental error with those found for other compounds.

The examination of NH_4NO_3, NH_4Cl, and NH_4Br indicates that the NH_4^+ ion behaves as if it were a metallic ion which gives rise to the negative adsorption. Therefore when the ammonia NH_3 is dissolved in water,[11] the NH_3 molecule is adsorbed at the surface of water forming a hydrogen bond with a water molecule, and the NH_3^+ ion is not formed by the capture of hydrogen ions in water. This is a very interesting conclusion which we can derive from the above experimental data.

As is clearly indicated in Table 1, the values found for $\Delta\gamma$ due to the hydrogen bond agree very well within the experimental error. This fact strongly supports the assumptions which we have stated at the beginning of the paper. Thus the anomaly of the surface tension exhibited by inorganic acids can be attributed to the hydrogen-bond formation at the surface of water.

In conclusion, the author wishes to express his thanks to Professor H. Erikson for his kind encouragement.

A Note on the Theory of Surface Tension of Ternary Solutions.

By Kyozo ARIYAMA.

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The present author has recently proposed a theory of surface tension of dilute solution of strong electrolyte,[1] and in the succeeding papers[2],[3],[4] the theory is extended to include the case of ternary solutions. More recently he has developed a theory of surface tension of aqueous solutions of inorganic acids.[5] If we have experimental data on the surface tension of ternary solutions of inorganic salt and inorganic acid, we will have a very interesting test on those theories in addition to those experimental tests which have been dealt with previously. Belton recently in his series of papers has given the experimental data on such ternary solutions.[6]

Since the surface tension of 0.1 mol hydrochloric acid is only 0.02 dynes/cm. less than that of water, it might be expected that its presence in strong solutions of salts could therefore be neglected. This would be so if the surface tension change for the mixture were the sum of the changes each solute would produce if present separately. This simple additive relation does not result however, and the effect of hydrocholoric acid increases with increasing salt concentration. Belton[6] confirmed this result with many solutions using many salts. A few examples of his results are given in the Table 1. In this Table the ratio $\Gamma_1/_0\Gamma_1$ stands for the ratio of the negative adsorption of the salt when the hydrocholoric acid is added to the negative adsorption of the salt when present alone in water.[4] This ratio was found to be less than one always.

This experimental fact can be accounted for theoretically by the theories mentioned above if the dielectric constant of adsorption layer is shown to be smaller than that of pure water when the inorganic acid is added.[4] We have no way of measuring the dielectric constant of the adsorption layer at present, but we can estimate it quite reasonably in the following way. When the hydrogen ions from inorganic acid are

(1) K. Ariyama, this Bulletin, **11** (1936), 687.
(2) *Ibid.*, **12** (1937), 32. (3) *Ibid.*, **12** (1937), 38. (4) *Ibid.*, **12** (1937), 44.
(5) *Ibid.*, **12** (1937), 109.
(6) Belton, *Trans. Faraday Soc.*, **31** (1935), 1413; **32** (1936), 1717.

positively adsorbed at the surface forming the hydrogen bond with water molecules,[5] the molecules of water will be of the structure similar to ammonia molecules having three hydrogen attached to three corners of the tetrahedron. Some water molecules at the surface may carry even four hydrogen atoms on the four corners of their tetrahedrons due to the hydrogen bond. As the number of such ammonia-like water molecules increases the dielectric constant of water is expected to decrease at the surface due to the following reasons.

The H_2O molecule is of the neon type with ten electrons as are also CH_4, NH_3, and FH. The dielectric constants for these substances as well as some other similar compounds are listed in the Table 2. It is clear

Table 1.

NaCl	HCl	$\Gamma_1/_0\Gamma_1$	KCl	HCl	$\Gamma_1/_0\Gamma_2$
m_1	m_2		m_1	m_2	
1	0.1	0.91	1	0.1	0.95
2	0.1	0.91	2	0.1	0.95
3	0.1	0.91	3	0.1	0.95
4	0.1	0.91	4	0.1	0.95
5	0.1	0.91			

Table 2.

	Dielectric constant		Dielectric constant
CH_4	2.3	PH_3	—
NH_3	25.4	SH_2	5.92
OH_2	80.	ClH	8.85
FH	83.5	HOOH	92.8

from this Table that as the number of hydrogen increases in molecule, the dielectric constant decreases. Thus it may be reasonable to expect that the ammonia-like water molecules will have a dielectric constant approximately the same as that of ammonia. If the number of such ammonia-like water molecules increases at the surface, it is reasonable to suppose that the dielectric constant of the adsorption layer is decreased from that of water.

Thus we can explain at least qualitatively Belton's experiments very easily.

Since it is very difficult to consider that the dielectric constant of adsorption layer is increased by the addition of inorganic acid in salt solution, the theories of the negative adsorption proposed by various other workers[7] seem to be unacceptable since they give a reverse result of the theory of the peresnt author.

In conclusion, author wishes to express his thanks to Dr. H. Erikson for his interest in the work.

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The Formation of *l*-Threose.

By Koichi IWADARE, Shozo FUKUNAGA, and Bennosuke KUBOTA.

(Received January, 25th, 1937.)

Obtaining *l*-threose by Wohl's method of degradation of *l*-xylose which was prepared from *l*-gulonolactone, Deulofeu[1] reported its specific rotation as to the left. It was, however, reported by R. Hockett[2] that the specific rotation of *d*-threose prepared by the Wohl degradation of *d*-xylose was lævorotation of $-12.5°$ in equilibrium. Hockett was thus forced to the conclusion that Deulofeu did not have pure substance and that the *l*-isomer should obviously have dextrorotation of equal numerical value with his *d*-isomer. The formation of *l*-threose, therefore, has not yet been accepted.[3]

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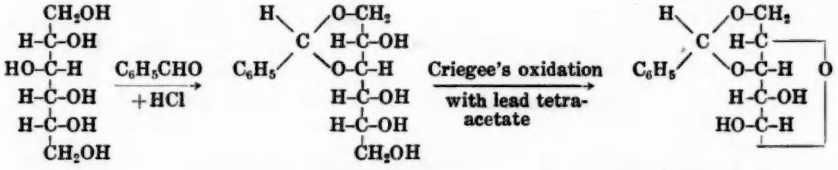
(7) Wagner, *Physik, Z.*, **25** (1924), 474; Shiba, *Bull. Inst. Phys. Chem. Research* (Tokyo), **13** (1934), 109; Onsagar and Samaras, *J. Chem. Phys.*, **2** (1934), 529.

(1) Deulofeu, *J. Chem. Soc.*, **1929**, 2458; *J. Am. Chem. Soc.*, **58** (1936), 855.

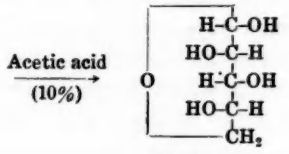
(2) R. Hockett, *J. Am. Chem. Soc.*, **57** (1935), 2265.

(3) See H. Vogel and A. Georg, "Tabellen der Zucker," (1931).

In the course of our investigation of monoses[4], we prepared, for the purpose of formation of *l*-talonic acid, a considerable quantity of *l*-galactonic acid, which is easily degraded to *l*-lyxose. In the hope of ascertaining the properties of *l*-threose, we made attempts to degrade *l*-lyxose to *l*-threose and to isolate it. Meanwhile we found that *l*-xylose was obtained very conveniently from *d*-sorbitol by Vargha's method[5]. This can be used as well as *l*-lyxose in obtaining *l*-threose and it was thus used as a starting material of this investigation, and the process of the reaction is shown in the scheme below.



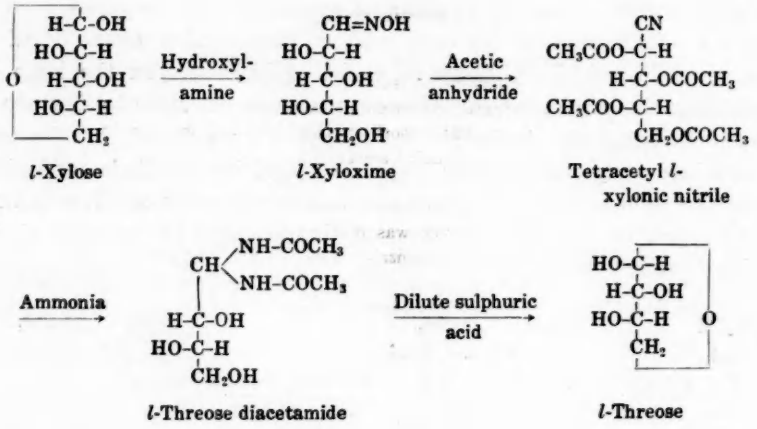
d-Sorbitol — 1,3-Monobenzal-*d*-sorbitol — 3,5-Benzal-*l*-xylofuranose



β-*l*-Xylose

l-Xylose thus obtained melts at 143° and rotates in equilibrium 18.2° to the left. Following the method of Deulofeu, it was submitted to degradation to *l*-threose by the method of Wohl. Being treated with hydroxylamine hydrochloride and sodium methylate, it changed into a thick syrup which consists mainly of *l*-xyloxime. When the *l*-xyloxime was warmed with acetic anhydride and sodium acetate in dioxane, a precipitate of tetracetyl-*l*-xylonic nitrile melting at 82° separated out. It was then decomposed with ammonia, and a colourless crystalline substance melting at 164–165°, the composition of which was $C_8H_{16}O_5N_2$, was obtained. It is nothing but *l*-threose diacetamide, and it rotates 10.8° to the right in water solution. Hockett's *d*-isomer rotates 10.9° to the left.

(4) S. Fukunaga, *J. Chem. Soc. Japan*, **57** (1936), 551.
(5) L. v. Vargha, *Ber.*, **68** (1935), 18.



l-Xylose — *l*-Xyloxime — Tetracetyl *l*-xylonic nitrile

l-Threose diacetamide — *l*-Threose

The equilibrium rotation of the sugar itself was determined with two solutions which were prepared by two different kinds of hydrolysis. The one solution which was prepared by hydrolysing *l*-threose diacetamide with 1/3 N sulphuric acid as in Deulofeu's experiment, rotated 13.2° to the right. The other which was prepared by hydrolysis with 1/10 N sulphuric acid and whose degree of hydrolysis was observed quantitatively as in Hockett's experiment, rotated also 13.1° to the right. The values obtained through these two observations show an almost satisfactory agreement. So we came to the conclusion that *l*-threose diacetamide could be completely hydrolysed with 1/3 N sulphuric acid.

Comparing, as shown below, the properties of *l*-threose and its derivative we obtained with those of Hockett's *d*-isomer, it seems to us that the two sugars are almost in good agreement as *d*- and *l*-isomer, and it seems to be clear that pure *l*-threose and its derivative are now formed, although Deulofeu could not have them from *l*-gulonolactone.

	Melting point of threose diacetamide	Specific rotation of threose diacetamide	Equilibrium specific rotation of threose
Deulofeu's *l*-threose	165–166°	−7.68°	−24.6°
Hockett's *d*-threose	165–167°	−10.9°	−12.5°
Authors' *l*-threose	164–165°	+10.8°	+13.1°

Experimental.

l-Xylose. This substance was obtained by a method which was recently published by Vargha. That is, 1 kg. of *d*-sorbitol, dissolved in one litre of water, was mechanically shaken with 100 c.c. of concentrated hydrochloric acid and 500 g. of benzaldehyde for 5–6 hours in a cool place. Monobenzal-*d*-sorbitol thus obtained was recrystallised from absolute alcohol and suspended in glacial acetic acid with equivalent tetracetyl lead. The mixture was shaken for an hour and the resulting almost clear solution was evaporated up in vacuo, and the syrup thus obtained was dissolved in ethyl acetate and water, and the ethyl acetate layer was distilled in vacuo to remove the solvent, and the resulting thick syrup of monobenzal-*l*-xylose was hydrolysed with 10% acetic acid. The syrup, obtained by distilling off the solvent under diminished pressure, was dissolved in a little water, charcoal added, and filtered. The solution was again evaporated under diminished pressure, and the remaining syrup or the impure crystal of *l*-xylose was recrystallised from alcohol. Melting point, 143°.

Its rotation in water was:

15 minutes after dissolution	$[\alpha]_D^{20} = -38.6°$;
63 minutes after dissolution	„ $= -18.4°$;
ca. 20 hours after dissolution (equilibrium)	„ $= -18.2°$.

Melting point of *l*-xylosazone, 163°.

The method devised by Wohl was selected for degrading *l*-xylose to *l*-threose, because both Hockett and Deulofeu used this method for degradation.

Tetracetyl-l-xylonic nitrile. *l*-Xylose (50 g.) was added to the neutral solution of hydroxylamine, which was made by neutralising 30 g. of hydroxylamine hydrochloride with sodium methylate. The mixture was warmed a little to dissolve the sugar after two days' standing and filtered. The filtrate was concentrated under diminished pressure to a thick syrup, keeping the outer bath under 50°, a little dioxane was added, and reconcentrated. Then 15 g. of recently fused sodium acetate and 30 c.c. of dioxane were added. The mixture was warmed a little, 10 c.c. of acetic anhydride added, and shaken vigorously. When spontaneous heating was ended, 10 c.c. more of acetic anhydride was added. This was repeated ten times. Then the mixture was warmed on a water bath for an hour and poured over cracked ice. A little sodium bicarbonate was added to partially neutralise the acetic acid, and the precipitate was filtered. It was recrystallised from absolute alcohol. Melting point, 82°.

l-Threose diacetamide. To 25 g. of tetracetyl-*l*-xylonic nitrile, 300 c.c. of ammonia was added. The mixture was warmed a little to dissolve the solid material, and, after three hours' standing, concentrated to syrup under diminished pressure. Then again ammonia was added and reconcentrated. The resulting syrup was dissolved in absolute alcohol, and a little ether was added. After two days' standing in refrigerator, the precipitated *l*-threose diacetamide was filtered. It was recrystallised several times from 85% alcohol, adding charcoal to remove gummy substance and colour. Then sharp needles separated very slowly. Melting point, 164–165° (corr.): $[\alpha]_D^{20} = +10.8°$. (Found: N, 12.69. Calculated for $C_6H_{10}O_5N_2$: N, 12.72%).

Equilibrium rotation of l-threose. To get the equilibrium rotation of *l*-threose, we performed two kinds of hydrolysis by using sulphuric acid of different concentra-

tions. Firstly, 0.3067 g. of *l*-threose diacetamide was made up to 10 c.c. with 1/3 N sulphuric acid. The solution was heated in a boiling water bath for three quarters of an hour. Thus we got the specific rotation of +13.2° (calculated from the weight of *l*-threose formed, the direct reading being +0.22° at 20°C.). This method is almost the same as Deulofeu's. Secondly, just as Hockett did, 0.2036 g. of *l*-threose diacetamide was made up to 10 c.c. with 0.100 N sulphuric acid. The solution was heated in a boiling water bath for 150 minutes, and 5 c.c. of it was titrated by Cajori's iodine oxidation method. This showed that, in 10 c.c. of the solution, 0.0913 g. of threose was formed by hydrolysis, and so 0.0362 g. of *l*-threose diacetamide remained unhydrolysed. The rotation of the hydrolysed solution was +0.16° in 10 cm. tube at 20°C. And the specific rotation calculated from these is +13.1°. The two values thus obtained showed an excellent agreement.

l-Threose. The sulphuric acid solution of *l*-threose was extracted with ether fifteen times to remove acetic acid, almost neutralised with barium hydroxide and then excess of barium carbonate and charcoal were added. The mixture was warmed on a water bath for a short while, and filtered. The filtrate was evaporated in vacuo to a thick syrup, and the latter was taken in absolute alcohol. The solution was filtered from inorganic impurities and evaporated. Thus the syrup of *l*-threose was obtained. But it did not crystallise on standing in a desiccator. To prepare the osazone, a portion of the syrup of *l*-threose was dissolved in a little water, and phenylhydrazine and acetic acid were added to it. The mixture was heated on a boiling water bath for about three hours. The precipitated *l*-threosazone (*l*-erythrosazone) was washed with a little benzene, and recrystallised from dilute alcohol. Yellow needles. Melting point, 162–163°.

Summary.

(1) *l*-Threose diacetamide has been obtained by the Wohl's method of degrading sugars from *l*-xylose which was prepared from *d*-sorbitol by Vargha's method.

(2) It has been found that this *l*-threose diacetamide melts at 164–165° (corr.) and has a specific dextrorotation of +10.8° in water. These properties are in good harmony with R. Hockett's value and sign, and do not agree with those of Deulofeu.

(3) This *l*-threose diacetamide has been submitted to hydrolysis with 1/3 N and 1/10 N sulphuric acid respectively. From these experiments the equilibrium specific rotation of *l*-threose in dilute sulphuric acid was determined to be +13.1°. It has a little higher value (about 0.6°) compared with Hockett's *d*-isomer, but it is now clear that the pure *l*-threose expected by Hockett has been obtained.

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Catalytic Hydrogenation of Amides of α-Hydroxy-Acids.[1]

By Haruomi ÔEDA.

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Several papers have been published on the reduction of acid amides. Reduction hitherto described are brought about by means of sodium, sodium amalgam or catalytic hydrogenation. The reaction goes along, according to the nature of amides in question and to the mode of reduction adopted, in two different directions as follows:

(I)[2] Amides are converted into alcohols, amino-groups being detached as ammonia:

$$R\cdot CO\cdot NH_2 \xrightarrow{4H} R\cdot CH_2\cdot OH + NH_3,$$

or (II)[3] converted into amines, with the formation of water:

$$R\cdot CO\cdot NH_2 \xrightarrow{4H} R\cdot CH_2\cdot NH_2 + H_2O.$$

Recently H. Adkins and B. Wojcik[4] have succeeded in preparing various amines by catalytic hydrogenation of amides with such a fair yield as had not been recorded in preceding reports. In unsubstituted amides, it is reported that the combined yields of primary and secondary amines amounted to 80–95%.

The present study was tried with the object of obtaining α-amino-alcohols from amides of α-hydroxy-acids in the same experimental conditions as in the works of Adkins. Hydrogenation was carried out in the presence of copper-chromium oxides at the temperature of 250°, initial pressure of hydrogen being 100–110 atmospheres at room temperature and dioxane was used as reaction medium. The present results carried out with two aliphatic amides (lactamide and leucic acid amide), however, are contrary to the expectation; and they never gave rise to α-amino-alcohols.

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(1) Studies on Hydroxy-acids and their Derivatives. V.

(2) Guareschi, *Ber.*, **7** (1874), 1462; Bouveault and Blanc, *Compt. rend.*, **138** (1904), 148.

(3) Guerbet, *Chem. Zentr.*, **70** (1899), II, 623; Sabatier and Maihe, *Ann. chim.*, [8], **16** (1909), 70.

(4) *J. Am. Chem. Soc.*, **56** (1934), 2419. Adkins described one case of hydroxy-amide. γ-Hydroxy-valeramide, on hydrogenation, gave some 4-hydroxy-1-aminopentane, while for the most part, it was recovered as valerolactone.

From both amides, neutral as well as basic substances were isolated by distillation of hydrogenated products. The former were found to be propylene glycol and isohexylene glycol, which were identified as such by preparing their phenylurethanes.

From leucic acid amide, an amine was obtained, whose boiling point is almost the same as that of the corresponding amino-alcohol. But the base easily solidifies (m.p. 62–64°) and the properties of its derivatives are not concordant with those of the amino-alcohol as shown in Table 1.

Table 1.

	HCl salt decomp. p.	Pt double choride decomp. p.	Benzoyl comp. m.p.	Picrate decomp. p.
Amine from C_6-amide	over 330°	over 330°	223–224° (corr.)	about 245°
$(CH_3)_2CH\cdot CH_2\cdot \underset{OH}{CH}\cdot CH_2\cdot NH_2$[5]	175°	215°	128°	—

The analytical results of the free base and of every derivative tabulated closely resemble the value calculated for $C_6H_{13}\cdot NH_2$, but the base, viewed from its properties, can never be regarded as isohexylamine (e.g. discrepancy of boiling points: the difference attains to 100°). Molecular weight of the free base, determined by Rast's method, is equivalent nearly to the double that of hexylamine. From these facts, the base is concluded to be the following diprimary-diamine:

$(CH_3)_2CH\cdot CH_2\cdot CH\cdot CH_2\cdot NH_2$
$(CH_3)_2CH\cdot CH_2\cdot \underset{}{CH}\cdot CH_2\cdot NH_2$ 2,3-Di-isobutyl-tetramethylene diamine.

From lactamide a liquid base was obtained. As it could not be isolated as hydrochloride in crystalline state, the base was converted into picrate. But the picrate was found to be a mixture and an attempt was made to separate them by recrystallisation from hot glacial acetic acid. The base (A in Table 2) of the picrate less soluble in the hot solvent was identified as the following diprimary-diamine by converting it into benzoyl compound:

$CH_3\cdot CH\cdot CH_2\cdot NH_2$
$CH_3\cdot \underset{}{CH}\cdot CH_2\cdot NH_2$ 2,3-Dimethyl-tetramethylene diamine.

(5) Mousset, *J. Chem. Soc.*, **82** (1902), I, 254; Kanao, *J. Pharm. Soc. Japan*, **49** (1929), 173.

Table 2.

		Picrate decomp. p.	Benzoyl comp. m.p.	Pt double chloride decomp. p.
Amine for C_5-amide	A	over 260°	227–228° (corr.)	—
	B	about 238°	—	265–270°
$CH_3 \cdot \underset{\underset{OH}{|}}{CH} \cdot CH_2 \cdot NH_2$[6]		142°	87°	195°

The other base B, whose picrate is more soluble, could not be definitely determined, as it does not give solid benzoyl compound, but the analytical data of the picrate as well as of the platinum double chloride coincide with those of the following primary-secondary-diamine:

$$\begin{matrix} CH_3 \cdot CH \cdot CH_2 \cdot NH_2 \\ | \\ CH_3 \cdot CH \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot CH_3 \end{matrix}$$ *N*-Propyl-2,3-dimethyl-tetramethylene diamine.

No information of these diamines was found in literature. They are the first substances obtained, which belong to 2,3-dialkyl derivatives of tetramethylene diamine.

From both amides, besides glycol and diamine, the higher boiling fractions were obtained in considerable quantity. All attempts to prepare crystalline derivatives from these fractions were unsuccessful.

The above hydrogenation can be regarded as the two known types of reduction of amides occurring side by side:

$$R \cdot \underset{\underset{OH}{|}}{CH} \cdot CO \cdot NH_2 \begin{cases} \nearrow & R \cdot \underset{\underset{OH}{|}}{CH} \cdot CH_2 \cdot OH + NH_3 \\ \searrow & R \cdot \underset{\underset{R \cdot CH \cdot CH_2 \cdot NH_2}{|}}{CH} \cdot CH_2 \cdot NH_2 + H_2O. \end{cases}$$

In reduction to amines, these amides do not give amino-alcohols, but they are transformed into diamines by the elimination of two hydroxyls by further reduction.[7]

(6) Peeters, *Rec. trav. chim.*, **20** (1901), 264; Gabriel and Ohle, *Ber.*, **50** (1917), 808.

(7) An example of the similar condensation, taking place in hydroxy-groups, is described in the formation of bis-camphorylethane by the reduction (with sodium) of camphoryl carbinol. Rupe and Ackermann, *Helv. Chim. Acta*, **2** (1919), 221.

$$C_8H_{14}\begin{matrix} CO \\ | \\ CH \cdot CH_2 \cdot OH \end{matrix} \rightarrow C_8H_{14}\begin{matrix} CO \\ | \\ CH \cdot CH_2 \cdot CH_2 \cdot CH \end{matrix}\begin{matrix} CO \\ | \\ \end{matrix}C_8H_{14}$$

Experimental.

Copper-chromium oxide catalyser (containing a little barium) was prepared according to Adkins.[8] Acid amides[9] were mixed with 1/4–1/5 parts of the above catalyser and diluted with four times of its weight of distille l (over sodium) dioxane. The hydrogenation was carried out in the same conditions as described in the previous paper.[10]

Hydrogenated products were separated from catalyser with glass filter and dioxane was removed by distillation through Widmer column. The residue was fractionated in vacuum into several fractions again with the aid of Widmer column.

Hydrogenation of Amide of *l*-Leucic acid.

Amide (m.p. 82–83°) 24 g. (0.18 mol); dioxane 75 c.c.; catalyser 5.0 g.; time of hydrogenation 2.5 hrs. at 245–255°; fractionation:

I	110–120° under 14 mm.	4.4 g.
II	120–130° ,,	3.2 g.
III	over 140° ,,	7.5 g.

Fraction II has the tendency to solidify instantly in the delivery tube, and to prevent the blockade, hot water must be circulated through the jacket. Fraction III, on the contrary, does not solidify and remains as yellowish viscous fluid even after long standing.

(A) Neutral Part (Isohexylene glycol). Fraction I was separated into neutral and basic parts by extracting the acidified mixture with ether as usual. The neutral part distilled at 109–111° under 13 mm. after refractionation. (The same neutral part was also obtained from fraction III by the same treatment.) It was found to be isohexylene glycol and the combined yield amounted to 10 mol%.[11]

Bis-phenylurethane. Prepared from the glycol and phenyl isocyanate by heating at 120–130° for one hour, the urethane being precipitated by adding ligroin. After recrystallisation from ligroin-alcohol, it melted at 116.5–117.5° (corr.), no depression of melting point was observed when mixed with the specimen described in the previous paper, m.p. 117.5° (corr.).[10]

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(8) *J. Am. Chem. Soc.*, **54** (1932), 1139.

(9) Leucic acid amide: prepared from liquid ammonia and acetone-leucic acid at −33°. Lactamide: from liquid ammonia and ethyl lactate at room temperature. Ôeda, this Bulletin, **11** (1936), 385.

(10) Ôeda, this Bulletin, **10** (1935), 531.

(11) The activity of this glycol was not examined owing to its minute quantity. The same glycol obtained in the previous experiment was found to be active. The two glycols show the same boiling range and give the phenylurethane of the same m.p. Rotation was determined in a 1-dm. tube (5 c.c.). $d^{18.5}_{18.5} = 0.9506$; $[\alpha]^{14}_{D} = -0.23°/0.95 = -0.24°$. The sample may be partially racemised during hydrogenation.

(B) **Basic Part.** Hydrochlorides obtained from fractions I and II were combined and evaporated to dryness on water bath and extracted with hot alcohol, when 2.3 g. of the sample remained unextracted.

(a) **Hydrochloride Insoluble in Alcohol (2,3-Di-isobutyl-tetramethylene diamine).** The insoluble hydrochloride was dissolved in a large bulk of hot water, filtered and was concentrated on water bath. During evaporation, a colourless hydrochloride began to crystallise out while still hot before the solution was completely dried up. After being purified by repeated crystallisation, it became, on heating, gradually coloured at 300° but did not decompose up to 330°. (Found: N, 10.46; Cl, 26.00. Calculated for $C_{12}H_{28}N_2 \cdot 2HCl$: N, 10.25; Cl, 25.98%.) Yield 9 mol%.

Platinum double chloride. Insoluble in alcohol. It turned black at 270° but did not decompose up to 330°. (Found: Pt, 32.07. Calculated for $C_{12}H_{28}N_2 \cdot H_2PtCl_6$: Pt, 32.00%.)

Free base. When the insoluble hydrochloride was warmed with an excess of dilute caustic potash, an oil separated out, which crystallised on cooling. The free base thus prepared was dissolved in alcohol, and decolourised with charcoal. By evaporation of the solvent colourless base (m.p. about 60°) was obtained as main product. It can also be recrystallised from ligroin, m.p. 62–64° after drying over caustic soda. (Found: C, 72.24; H, 13.66; N, 14.22. Calculated for $C_{12}H_{28}N_2$: C, 71.94; H, 14.09; N, 14.00%.) *Optical rotation.* Determined in a 1-dm. tube (5 c.c.) containing 0.250 g. of the free base and made up to 5.00 c.c. with alcohol. No rotation was observed. *Molecular weight* (camphor): 208. Calculated for $C_{12}H_{28}N_2$: 202.

Benzoyl compound. To a suspension of the powdered free base in 15% caustic potash, benzoyl chloride was gradually added with constant stirring. An oil formed first, then turned to a crystalline sticky mass, which was separated by suction and washed with hydrochloric acid, sodium bicarbonate solution and finally with water. It melted at 223–224° (corr.) after recrystallisation from alcohol. (Found: C, 76.58; H, 9.26; N, 7.12. Calculated for $C_{20}H_{36}O_2N_2$: C, 76.42; H, 8.88; N, 6.86%.)

Picrate. Obtained by mixing alcoholic solutions of the free base and of picric acid in excess. After recrystallisation from alcohol, it turned black at 240° and decomposed at about 248° with violent evolution of gas. (Found: C, 43.99; H, 5.05; N, 17.27. Calculated for $C_{12}H_{28}N_2 \cdot 2C_6H_3O_7N_3$: C, 43.74; H, 5.20; N, 17.03%.)

(b) **Hydrochloride Soluble in Alcohol (A base left undetermined).** After recrystallisation from a little alcohol, powder of silky luster was obtained, it melted with decomposition at 220–230°. (Found: Cl, 18.94%. It corresponds to a free mono-amine, mol. wt. 151.[12]) Owing to the minute quantity of purified sample, further study was given up.

(C) **Higher Fraction.** Fraction III was fractionated through Widmer column. It distilled between 135–180° under 13 mm. and showed no distinct boiling fraction. It was dissolved in hydrochloric acid, and insoluble resinous matter was filtered off. The hydrochloride of the base could not be brought into crystallisation. A ferrocyanate, insoluble in water, was obtained from the above solution, but no further study on this line has been made.

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(12) Supposing the existence of a prim.-sec.-diamine, similar as in the case of lactamide, its molecular weight (calculated as mono-amine) will be: $\frac{1}{2}C_{18}H_{40}N_2 = 142$.

Hydrogenation of *dl*-Lactamide.

Amide (m.p. 77–78°) 14.5 g. (0.16 mol); dioxane 60 c.c.; catalyser 4.0 g.; time of hydrogenation, 3 hrs. at 240–255°; initial pressure of hydrogen 112 atms.; fractionation:

I	60 – 90°	under 20 mm.	0.9 g.
II	90 – 100°	,,	1.4 g.
III	over 100°	,,	2.2 g.

(A) Picrates from Fractions I and II. Obtained from the free base and a little excess of alcoholic picric acid. Yield, 1.9 g. from fraction I, 1.1 g. from II. The picrate is insoluble in water and alcohol, but partly soluble in hot glacial acetic acid. After washing completely with hot alcohol, it was extracted with hot glacial acetic acid, the residue being collected and again extracted with a new bulk of the solvent. The extraction was repeated until the amount of final residue decreased to one-tenth of the initial sample. The final residue so obtained is designated as picrate A. Each extract was cooled, the precipitated picrate being separately collected. The most soluble part (picrate B) was obtained by fractional crystallisation.

(a) **Picrate A.** Pale yellow amorphous powder. It showed no change in appearance up to 230–240°, and thereafter gradually coloured, but did not decompose up to 260°. The result of analysis is not actually identical with the value calculated for the diprimary-diamine. The discrepancy may be due to the incomplete separation of picrate B. (Found: C, 38.64, 38.78; H, 4.00, 3.42; N, 20.02. Calculated for $C_6H_{16}N_2 \cdot 2C_6H_3O_7N_3$: C, 37.61; H, 3.87; N, 19.50%.)

Benzoyl compound. The picrate was transformed into hydrochloride, from which benzoyl compound was prepared with benzoyl chloride in the presence of caustic potash. It separated as an oil, aqueous solution was removed by decantation, and the oil, on rubbing together with a little ether, yielded colourless crystals. Recrystallised from alcohol, it melted at 227–228° (corr.). (Found: C, 74.45; H, 7.46; N, 8.42. Calculated for $C_{20}H_{24}N_2$: C, 74.03; H, 7.47; N, 8.64%.)

(b) **Picrate B.** Yellow crystals. It decomposed at 237–240° with violent evolution of gas. (Found: C, 40.50, 40.34; H, 4.30, 3.70; N, 18.51. Calculated for prim.-sec.-diamine, $C_9H_{22}N_2 \cdot 2C_6H_3O_7N_3$: C, 40.88; H, 4.58; N, 18.17%.) The preparation of benzoyl compound was tried in similar way as above, but it could not be obtained in crystalline state.

Platinum double chloride. Obtained from the syrupy hydrochloride which was prepared from the above purified picrate. It decomposed at 265–270°. (Found: Pt, 34.50. Calculated for $C_9H_{22}N_2 \cdot H_2PtCl_6$: Pt, 34.33%.)

(B) Glycol. A little hydrochloric acid was added to another sample of fraction II and a neutral part was collected by extraction with a large bulk of ether. The extract distilled at 77–79° under 8 mm. It was found to be isohexylene glycol by converting it into bis-phenylurethane.

Bis-phenylurethane. Prepared from the glycol and phenyl isocyanate by heating at 120–130° for one hour. After recrystallisation from alcohol, it melted at 145–146° (corr.), alone or in admixture with the specimen (m.p. the same) described in the previous paper.[10]

The present study was carried out in the Chemical Institute, Faculty of Science, Imperial University of Tokyo. The author expresses his sincere thanks to Prof. K. Matsubara for kind inspection of this paper. His best thanks are also due to Dr. Y. Takayama for constant encouragement during this study.

Studies on the Oiliness of Liquids. IV. Measurements of the Static Friction Coefficients by the Method of Inclination.

By Jitsusaburo SAMESHIMA and Yasuji TSUBUKU.

(Received February 26th, 1937.)

The measurements of the static friction coefficients by the balance method have already been described in one of the former papers.[1] In the present paper, the method of inclination and the results obtained therefrom are described. The method is based on the measurement of the critical angle of inclination of the sliding surface at which the slider begins to slide.

Fig. 1 shows the apparatus. A and B are brass plates joined together with a hinge at one end C. The other end of the plate B can be lifted by rotating the handle D and pulling the string fastened to E. Thus the plate B is made to incline from the horizontal plane, the angle of inclination being measured by the protractor G.

H is a glass plate on which a microscopic slide glass K is placed. L is the slider made of an optical lens of the diameter 2.5 cm. M is the brass discs pasted on the slider, which is used to adjust the weight of the slider. N is the supporter to keep the slider from going too far.

At first the liquid is applied on K and then the slider is put on it, the plate B and the sliding surface K being in horizontal position. Now rotate the handle D gently and make the plate B inclines gradually, until finally the slider L begins to slide down the inclined plane. At this instant the angle of inclination is read by the protractor G.

(1) Sameshima, Kidokoro, and Akamatu, this Bulletin, **11** (1936), 659.

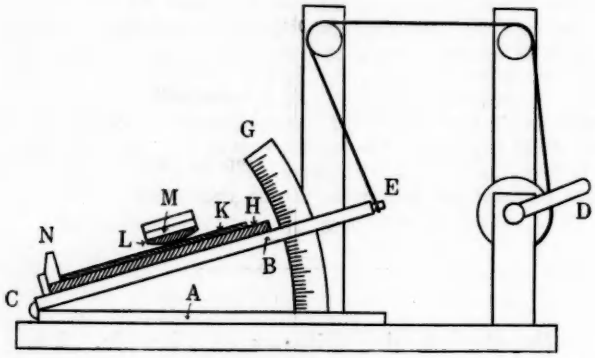

Fig. 1.

We shall denote the sliding angle with θ, the total weight of the slider and brass discs with w, and the force acting in the direction of parallel and normal to the sliding plane with F and W respectively. There are the relations:

$$F = w \sin\theta ,$$

$$W = w \cos\theta .$$

The friction coefficient μ is,

$$\mu = \frac{F}{W} = \tan\theta .$$

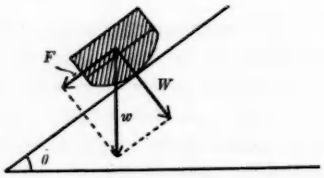

Fig. 2.

These relations are shown in Fig. 2.

The sliding angle θ decreases with increasing value of w when the weight of slider w is small. If w is sufficiently large, however, the angle θ is practically independent of w. The friction coefficient μ is to be calculated from such a constant sliding angle θ. The results of measurements are summarized in Table 1. The experiments have been done at the room temperature of 20–24°C.

The values of friction coefficient μ against the number of carbon atoms in the molecules are plotted in Fig. 3 and Fig. 4.

From Fig. 3 we see that the friction coefficients of aliphatic acids are nearly constant, while those of aliphatic alcohols diminish with the number of carbon atoms in their molecular formula. These facts have already been noticed in the results of the previous experiments.[2] We might

(2) Sameshima, Kidokoro, and Akamatu, this Bulletin, **11** (1936), 666.

Table 1.

Lubricant	w (g.)	$\tan\theta$	μ
Methyl alcohol CH_3OH	32	0.81	
	42	0.77	
	52	0.72	
	62	0.68	
	72	0.66	0.66
	82	0.66	
Ethyl alcohol C_2H_5OH	52	0.74	
	62	0.68	
	72	0.65	0.65
	82	0.65	
n-Propyl alcohol $CH_3(CH_2)_2OH$	52	0.67	
	62	0.66	
	72	0.64	0.635
	82	0.63	
n-Butyl alcohol $CH_3(CH_2)_3OH$	62	0 71	
	72	0.69	
	82	0.66	
	92	0.65	
	102	0.63	0.63
n-Amyl alcohol $CH_3(CH_2)_4OH$	62	0.66	
	72	0.64	
	82	0.60	
	92	0.60	0.60
	102	0.60	
n-Hexyl alcohol $CH_3(CH_2)_5OH$	92	0.65	
	101	0.61	0.61
	111	0.61	
n-Heptyl alcohol $CH_3(CH_2)_6OH$	82	0.68	
	92	0.66	
	102	0.65	
	112	0.62	
	122	0.60	0.60
	132	0.60	
n-Octyl alcohol $CH_3(CH_2)_7OH$	91	0.64	
	101	0.59	
	111	0.59	
	121	0.58	0.58
	131	0.58	
Acetic acid CH_3COOH	82	0.65	
	91.9	0.63	
	101.5	0.59	
	111.1	0.59	0.59
	121.1	0.59	
	131.2	0.59	

Lubricant	w (g.)	$\tan\theta$	μ
Propionic acid CH_3CH_2COOH	101 5	0.63	
	111.1	0.60	
	121.1	0.59	
	131.2	0.59	0.59
	140.6	0.59	
n-Butyric acid $CH_3(CH_2)_2COOH$	111.1	0.64	
	120.9	0.62	
	131.0	0.60	0.60
	140.6	0.60	
n-Valeric acid $CH_3(CH_2)_3COOH$	111.1	0.61	
	120.9	0.60	0.60
	131.0	0.60	
Caproic acid $CH_3(CH_2)_4COOH$	111.1	0.59	
	120.9	0.59	
	131.0	0.58	0.58
	140.6	0.58	
Heptylic acid $CH_3(CH_2)_5COOH$	111.1	0.60	
	120.9	0.60	
	131.0	0.58	0.58
	140.6	0.58	
Caprylic acid $CH_3(CH_2)_6COOH$	111.1	0.59	
	120.9	0.57	
	131.0	0.55	0.55
	140.6	0.55	
Nonylic acid $CH_3(CH_2)_7COOH$	111.1	0.61	
	120.9	0.61	
	131.0	0.60	
	140.6	0.58	
	152.2	0.58	0.58
	162.3	0.58	
Oleic acid $C_{17}H_{33}COOH$	120.9	0.37	
	131.0	0.36	0.36
	140.6	0.36	
Water H_2O	32	0.82	
	42	0.76	
	52	0.73	
	62	0.69	
	71.5	0.65	0.65
	81.5	0.65	
	72	0.74	
	82.2	0.69	0.69
	92	0.69	
		Mean	0.67

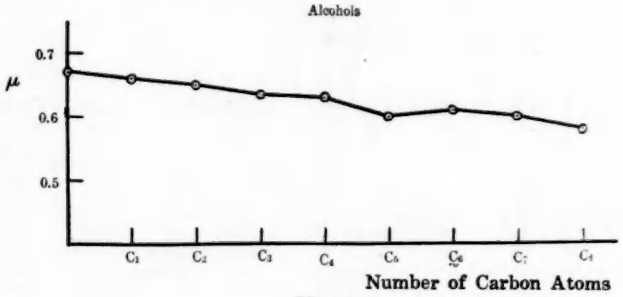

Fig. 3.

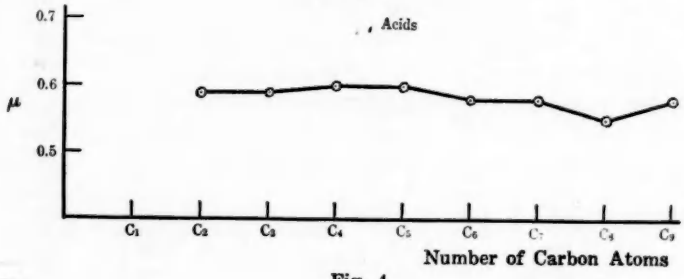

Fig. 4.

perhaps venture the following hypothesis to explain the observed results of the friction coefficient.

It has been proved that the coefficient of static boundary friction of the flooded liquid is practically the same with that of the monomolecular film of the substance.[3] So the friction coefficients obtained in the present experiments are considered to depend only on the properties of the monomolecular film attached to the glass surface.

The molecules of the aliphatic alcohols or the acids tested in the present experiments are composed from the hydrocarbon groups and the hydroxyl or carboxyl group, thus,

$$CH_3CH_2 \text{ ..... } CH_2(OH),$$

$$CH_3CH_2 \text{ ..... } CH_2(COOH).$$

The hydrocarbon group is nonpolar, while hydroxyl or carboxyl group polar. The molecules, therefore, will take orientation on the sliding surface, the polar group being attached to the glass surface. The attraction force between glass and COOH group will be stronger than that

(3) Akamatu and Sameshima, this Bulletin, **11** (1936), 791.

between glass and OH group, for the glass is an alkaline substance. The acid molecules, therefore, will stand more firmly on glass surface than alcohol molecules.

Fig. 5 shows the model of the molecules of acid and alcohol standing on the glass surface.

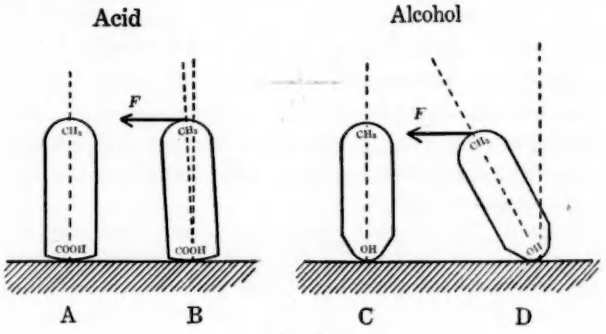

Fig. 5.

If the force F is applied at the heads, CH_3 group, of the molecules, then they will incline as shown in Fig. 5, B or D. The COOH or OH group will act as the hinge. The acid molecule has strong affinity with glass, or it may be considered that the hinge is stiff while alcohol molecule has weak affinity or the hinge is loose. So the acid molecule inclines in smaller angle by the force F than the alcohol molecule.

The force acting on the hinge point is the product of the pulling force and the length of the molecule. So the longer the molecule the greater is the angle of inclination of the molecule. Or the long molecule can be made incline at definite angle with the small pulling force. Thus the alcohols of long chain have small friction coefficients than those of short chain. The acid molecule, however, can hardly be made incline by the pulling force, as is shown in Fig. 5, B, so the friction coefficient is not practically change with the number of carbon atoms. If the length of molecule becomes very long, such as palmitic or stearic acid etc. then the force will act very strong on the COOH hinge and, moreover, the flexibility of the molecule may show some effect on the friction coefficient as is supposed by Adam[4] and others. In the present experiment, however, only comparatively short molecules are tested, so the flexibility of the molecule will not have serious effect on the friction coefficient.

(4) N. K. Adam, "The Physics and Chemistry of Surfaces," p. 227, Oxford (1930).

The lengths and the diameters of the molecule of octyl alcohol and nonylic acid are calculated as shown in Table 2.

Table 2.

Molecular formula	Density of liquid	Cross sectional area of molecule	Diameter of molecule	Length of molecule
$CH_3(CH_2)_7OH$	0.83	21.6 Å^2	4.6 Å	12.1 Å
$CH_3(CH_2)_7COOH$	0.91	20.5 Å^2	4.5 Å	14.1 Å

Thus the length of molecule is about three times of the diameter. So the molecule is comparatively short, and therefore, the molecule will not bend by the pulling force.

The expence of the present experiments has been defrayed from a grant given by Nippon Gakujutsu Shinkokwai (Japan Society for the Promotion of Scientific Research) for which the authors' sincere thanks are due.

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The OH-Vibration Spectrum in the Photographic Infrared.

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(Received March 1st, 1937.)

The result of our dipole measurement on ortho-substituted phenols[1] is in accordance with Pauling's theory[2] of quantum mechanical resonance, which was originally put forward for the interpretation of the infrared absorption spectra observed by Wulf and Liddel.[3] To supply further experimental evidence to this conclusion as well as to complete our former research[4] on the vibration spectra of alcohols, we have

(1) Mizushima, *J. Chem. Soc. Japan*, **57** (1936), 936; see also Mizushima, Morino, and co-workers, *Physik. Z.*, **35** (1934), 905; *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25** (1934), 159; **29** (1936), 63, 111, 188.

(2) Pauling, *J. Am. Chem. Soc.*, **58** (1936), 94.

(3) Wulf and Liddel, *J. Am. Chem. Soc.*, **57** (1935), 1464; Wulf, Liddel, and Hendricks, *ibid.*, **58** (1936), 2287.

(4) Mizushima, Morino, and Okamoto, this Bulletin, **11** (1936), 553, 698.

studied the overtones of the OH vibration as absorption spectra in the photographic infrared. The measurement was carried out with a glass spectrograph of our own construction which has a dispersion of 74 A per mm. at 9000 Å, iron and barium lines being used as reference. The samples were Kahlbaum's products, which were purified by redistillation or recrystallization. The accompanying table contains the experimental results obtained for carbon tetrachloride solutions of the concentration of 0.5 mol. We have also measured the absorption spectra in the pure liquid or fused state and found that some of the bands are changed in frequency as well as in intensity.[5] We shall, however, confine ourselves to the discussion of the experimental data obtained for the dilute nonpolar solutions, in which the normal vibration of a solute molecule is not greatly affected by the surrounding solvent molecules.[6]

Frequencies (cm.$^{-1}$) of Absorption Maxima of OH Vibration Bands.

(Solvent : CCl_4)

Substance	ν_2	ν_3	$x\omega$	ω	ν_1		D
					calc.	obs.	
CH_3OH	10424 (9593 Å)	13557 (7376 Å)	85	3816	7120	7120	116
C_2H_5OH	10394 (9621 Å)	13493 (7411 Å)	91	3830	7112	7090	109
n-C_3H_7OH	10388 (9626 Å)	13493 (7411 Å)	89	3820	7104		111
n-C_4H_9OH	10406 (9610 Å)	13459 (7430 Å)	104	3884	7144		98
C_6H_5OH	10332 (9679 Å)	13430 (7446 Å)	87	3790	7061	7050	113
p-C_6H_4ClOH	10322 (9688 Å)	13430 (7446 Å)	83	3773	7047		116
o-C_6H_4ClOH	10094 (9907 Å) st.*	13122 (7621 Å) st.	84	3701	6897	6910	110
	10323 (9687 Å) w.	13430 (7446 Å) w.	84	3775	7049	7050	116
o-C_6H_4BrOH	10005 (9995 Å) st.	12970 (7710 Å) st.	93	3705	6855	6860	100
	10328 (9682 Å) w.	13401 (7462 Å) w.	92	3812	7070	7050	106
o-$C_6H_4CH_3OH$	10328 (9682 Å)	13430 (7446 Å)	85	3783	7055	7060	114

* st. means strong intensity and w. weak intensity.

(5) Measurements with alcohols in the pure liquid state were already carried out by several investigators, among which Freymann (Thèse Paris, 1933) gave experimental values close to those of our second overtones.

(6) The absorption bands at 9500Å of alcohols in the vapour state recently observed by Badger and Bauer (*J. Chem. Phys.*, **4** (1936), 711) have larger frequencies owing to the difference in the state of aggregation.

Let the vibrational level of the quantum number v be approximately expressed as

$$G(v) = \omega\left(v+\frac{1}{2}\right)-x\omega\left(v+\frac{1}{2}\right)^2 \qquad (1)$$

Then the frequency of infinitesimal vibration ω and the anharmonicity factor x can be calculated, if we assign our observed bands to the second (ν_2) and third overtones (ν_3) of the OH vibration respectively. Using the values of ω and x *thus* evaluated, we have calculated the frequencies of the first overtone (ν_1) and compared them with the experimental values which Wulf and his co-workers[8] obtained in the same solution (sixth column of the table). The agreement is satisfactory within the limit of experimental error, so that the assignment of the absorption bands given above is proved to be correct.

By the extrapolation method the dissociation energy is calculated as

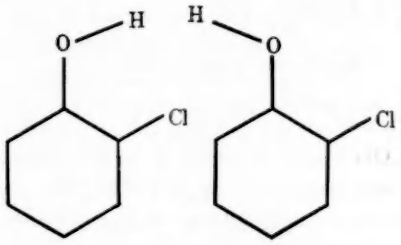
$$D = \frac{(\omega-x\omega)^2}{4x\omega} \qquad (2)$$

which we can now evaluate by the use of ω and x given in the table. The calculated values (in Kcal.) shown in the last column of the table are in good agreement with those obtained from the thermochemical data (106 Kcal. for alcohols). Of course the comparison between these two kinds of dissociation energy is of no significance, if there is any complication of the electronic levels such as the crossing of them, but for these substances such does not seem to be actually the case.

Thus the experimental results obtained here together with all the other evidence available at present are consistent with the interpretation of these spectra to be due to one normal mode of vibration of the molecule, which is essentially the vibration of the hydrogen atom of the OH radical relative to the rest of the molecule. The two frequencies observed in all of the overtones for the ortho-halogenated phenols can therefore be ascribed to the stereoisomers I and II respectively,[7] which owe their existence to the quantum mechanical resonance between single and double bonds

(7) The frequency which is approximately equal to that of phenol is assigned to the isomer II, in which the OH vibration is not affected by the halogen atom appreciably.

as suggested first by Pauling.[2] The absorption intensity for I is much larger than that for II, indicating that the number of molecules of the type I is much larger than that for II in conformity with the experimental result obtained in the dipole measurement.[1]



(I) (II)

We have also observed a very interesting fact that the absorption intensity due to the OH vibration becomes very strong as compared with that due to the CH vibration in the dilute CCl_4 solution, while both of them do not seem much different in the pure liquid state.[8] This can be explained by assuming the association caused by hydrogen bond, which has a large effect in decreasing the intensity of a vibration spectrum.[9] Owing to the large difference in the polar character the inherent absorption intensity of the OH vibration must be much larger than that of the CH vibration as was actually observed in the dilute non-polar solutions, but the considerable formation of hydrogen bond in the pure liquid state decreases the intensity of the former, so that it becomes comparable with (in some cases weaker than) that of the latter.

We thank Prof. M. Katayama for his kind advices. Our thanks are also due to Dr. K. Nagaoka (Rokuôsha), who supplied us with the infrared plates. We are indebted to Hattori-Hôkôkai for a grant in aid of this research.

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(8) In some cases the absorption due to the CH vibration is much stronger than that due to the OH vibration in the pure liquid state.

(9) For o-nitrophenol we could not observe the second and third overtones of the OH vibration, just as Wulf and Liddel did not in the first overtone. This is ascribed to the formation of a hydrogen bond.[3]

A Note on the Polymerisation of Styrene as revealed by the Raman Effect.

By San-ichiro MIZUSHIMA, Yonezo MORINO, and Yoshiki INOUE.

(Received March 5th, 1937.)

The polymerisation of styrene is considered to proceed by the opening of the double bonds of monomeric molecules $C_6H_5CH = CH_2$ to form macromolecules.(1) Signer and Weiler applied the Raman effect to prove this polymerisation mechanism,(2) showing that the Raman line due to the presence of a double bond disappeared in the polymerisation product. If we assume, as Staudinger and Steinhofer(3) considered, that the terminal valency of the long thread molecule acquires a double bond, we cannot expect the complete disappearance of the said line for polystyrene. It would, however, be very difficult in the case of Signer's experiment to prove the existence of this line, the intensity of which must be very small owing to the high molecular weight (40000) of the sample used. For this reason we have carried out an intensity measurement on the Raman lines of polystyrene having a lower polymerisation degree according to the method described in our previous communication.(4) For a polymer,(5) for which the cryoscopic measurement (in benzene solution) gave a molecular weight of 1150, the intensity of the line 1602 was found to be five times as large as that of the line 1634, while for the monomer the latter was twice as strong as the former; so that the line 1634 decreased in intensity by 1/10 relatively to the line 1602, when about 11 molecules in the mean polymerised to form one long molecule. If we assume quite simply that the intensities of the lines of 1634 and 1602 are proportional to the number of ethylene bonds and benzene nuclei respectively, the observed intensity change can conform with the view that polystyrene does not consist of ring molecules but of thread molecules which have ethylene bonds as the terminal valency.(3)

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(1) Staudinger, "Die hochmolekularen organischen Verbindungen", Berlin, (1932).

(2) Signer and Weiler, *Helv. Chim. Acta*, **15** (1932), 649.

(3) Staudinger and Steinhofer, *Ann.*, **517** (1935), 35.

(4) Mizushima, Morino and Higasi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25** (1934), 159; see also *Physik. Z.*, **35** (1934), 905.

(5) The sample was prepared by heating the monomer at 130°C for ten hours.

We have also followed the polymerisation process at room temperature by means of such an intensity measurement and found that the viscosity of the sample changed considerably, before the intensity change was appreciable. Hence we must consider that the viscosity change is in some cases caused by the formation of micelle built up from small single molecules held together by the van der Waals force, but not by the formation of macromolecule in which all the atoms are linked together by electron pair bonds.

We thank Prof. M. Katayama for his kind advices. Our thanks are also due to Dr. S. Kimura who supplied us with the samples used in this experiment. We are indebted to Hattori-Hôkôkai for a grant in aid of this research.

Raman Lines of Styrene and Polystyrene.

Monomer	Polymer(6)	Monomer	Polymer
212 (1)	224 (2)	1204 (6)	
241 (3)		1240 (0)	
445 (1b)		1301 (1)	
510 (0)		1321 (3)	
558 (1)	558 (2)	1414 (6)	
621 (3)	622 (4)	1450 (0)	1450 (1)
	763 (1)	1496 (2)	
774 (4)		1555 (0)	
796 (0)	795 (1)	1575 (1)	1580 (1)
835 (0)	835 (0)	1601 (10)	1602 (10)
909 (2)	904 (0)	1632 (20)	1634 (2)
999 (9)	999 (12)	2909 (0)	
1035 (2)	1031 (3)		2930 (2)
1156 (2)	1156 (3b)	3009 (3)	
1183 (3)		3059 (7)	3050 (8)
	1197 (4b)		

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(6) For the polymer some of the weak lines might escape our observation owing to the inevitable background.

The Addition of Hydrogen Bromide to Allyl Bromide in the Presence of Various Substances. V. A Comparison of the Effect of Oxygen with That of Peroxide. The Relation between the Amount of Oxygen Present and the Result of Addition.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

(Received February 12th, 1937.)

Two groups of substances, oxygen and peroxides as one group and the ferro-magnetic metals as the other, have been found capable of not only inversing the proportion of 1,3-dibromopropane and 1,2-dibromopropane in the product from allyl bromide and hydrogen bromide but also increasing the total yield of the addition. While the catalytic action of the ferro-magnetic metals has been established exactly by the authors,[1] there has been no experimental evidence to decide whether the so-called peroxide effect is caused by oxygen or by peroxides or by both. But, as mentioned in the third paper of this series,[2] at least the effect by oxygen seems to be due to the action of molecular oxygen. The reason for it is given above all by the fact that the addition of hydrogen bromide to peroxide-free allyl bromide in the presence of oxygen in the dark gives mainly the abnormal addition product, 1,3-dibromopropane, while no peroxide can be formed from allyl bromide and oxygen in the dark as judged from the test with ammonium thiocyanate and ferrous ammonium sulphate, and hydrogen bromide can not be considered to facilitate the formation of a peroxide. The only possible alternative is to attribute the effect to a peroxide which might be formed even in the dark in such a minute quantity as not detected by the above-mentioned test.

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(1) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754; **12** (1937), 51.

(2) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 798.

Corrections to the third paper: All the numerical values of liberated bromine expressed in volumes of corresponding amounts of oxygen should be divided by 10. The mistakes were caused by errors in calculation. As the authors were then aware of some inevitable sources of errors involved in the estimation of bromine, they did not attach importance to the obtained figures, and discussions made in that paper and the conclusions drawn from them require no alteration nor modification. It has now become clear that only a small fraction of the oxygen in the air admitted into the reaction tube was consumed to oxidize hydrogen bromide in the presence of platinum black (exp. 1).

In Table 1 the results of additions to peroxide-containing allyl bromide in vacuum are compared with those of additions to peroxide-free allyl bromide in the presence of oxygen. Allyl bromide treated with oxygen was placed in diffused light for a few days for the formation of the peroxide. The peroxide content was determined by iodometry, assuming that all the oxygen atoms in the peroxide of allyl bromide are available for the oxidation of the iodide:

$$\begin{matrix} CH_2\text{-}CH\text{-}CH_2Br \\ O\text{—}O \end{matrix} + 4KI + 2H_2O = CH_2{=}CH\text{-}CH_2Br + 4KOH + 2I_2.$$

The allyl bromide (24 g.) was taken in a reaction tube (135–140 c.c.). The contents were frozen by cooling in liquid air and the tube was evacuated, dissolved, uncombined oxygen being removed by this process. Then hydrogen bromide was condensed while the reaction tube was cooled in solid carbon dioxide and chloroform until a volume increase corresponding to 20 g. of hydrogen bromide was reached (total volume of the liquid 27 c.c.). The tube was evacuated again under cooling in liquid air and sealed off without entrance of air. On the other hand, in a quite similar manner, another reaction tube was charged with peroxide-free allyl bromide and hydrogen bromide, a volume of oxygen corresponding to the above peroxide content (the available peroxidic oxygen and the molecular oxygen equal in the number of atoms) being admitted at sealing. The tubes were shaken at room temperature in the dark for three days. In order that the reaction may occur under the same conditions, the additions to be compared were carried out simultaneously. Thus additions belonging to the same series occurred at the same time.

As allyl bromide (commercial product distilled once) used in exp. 2–4 was found not pure later, it was redistilled for exp. 5. In exp. 6–8 portions from the same specimen of especially purified allyl bromide were employed. The influence of impurities on the catalytic action of oxygen will be discussed later, but for the present more weight may be attached to the experiments of Series III.

Exp. 4 and 7 were carried out to see how quickly the peroxide is decomposed by the action of hydrogen bromide, allyl bromide being treated with hydrogen bromide in the reaction tube at room temperature for a short time before cooling in liquid air. The peroxide is decomposed rather rapidly, if not instantaneously. In the third paper[2] it was shown that the peroxide is not decomposed by hydrogen bromide at the temperature of solid carbon dioxide and chloroform, and that uncombined oxygen is removed by evacuation under cooling in liquid air.

Table 1. Comparison of Oxygen and Peroxide.

Series of exp.	No. of exp.	Remarks	Product: Dibromopropanes			
			Yield (%)	Boiling point (°C/mm.)	1,3- (%)	1,2- (%)
I	1	Allyl bromide containing peroxide corresponding to 4.8 c.c. O_2 per 24 g.	52	44–53.5/12	87	13
	2	Peroxide-free allyl bromide. 4.8 c.c. O_2 admitted.	53	44–54/12	95	5
II	3	Allyl bromide containing peroxide corresponding to 0.9 c.c. O_2 per 24 g.	28	41–52.5/11	62	38
	4	The same allyl bromide as above, treated with HBr for 2 min. at room temp. and left to stand for 10 min. before condensing HBr.	16	36–49/11	26	74
	5	Peroxide-free allyl bromide. 0.9 c.c. O_2 admitted.	57	43–52.5/11	81	19
III	6	Allyl bromide containing peroxide corresponding to 0.8 c.c. O_2 per 24 g.	43	42–53.5/10	70	30
	7	The same allyl bromide as above, treated with HBr for 1 min. at room temp. and HBr condensed immediately.	35	41–53/10	65	35
	8	Peroxide-free allyl bromide. 0.8 c.c. O_2 admitted.	46	42–53.5/10	78	22

Experiments of each series were carried out simultaneously. The peroxide content of allyl bromide is given in the volume of the corresponding amount of oxygen for the temperature and pressure at which oxygen was taken in the run for comparison.

Table 2. Relation between the Amount of Oxygen Present and the Result of Addition.

Series of exp.	No. of exp.	Volume of oxygen admitted (c.c.)	Product: Dibromopropanes			
			Yield (%)	Boiling point (°C./mm.)	1,3- (%)	1,2- (%)
IV Purified allyl bromide. Time of reaction: 3 days.	9	0	14	32–36/10	4	96
	10	0.5	21	34–46/10	38	62
	11	1.5	44	42–51.5/9	95	5
	12	2.5	43	42–51.5/9	96	4
V Purified allyl bromide. Time of reaction: 5 days.	13	0	24	35–42/10	12	88
	14	0.5	37	37–51/10	60	40
	15	1.5	56	42–51.5/9	96	4
	16	2.5	62	42–51.5/9	96	4
VI Once distilled allyl bromide. Time of reaction: 5 days.	17	0	28	38–47/13	44	56
	18	0.5	64	45–56.5/13	89	11
	19	1.5	68	45–56.5/13	96	4
	20	2.5	73	45–56.5/.3	96	4

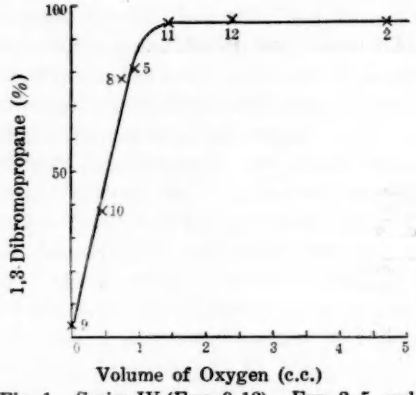

Fig. 1. Series IV (Exp. 9–12). Exp. 2, 5, and 8.

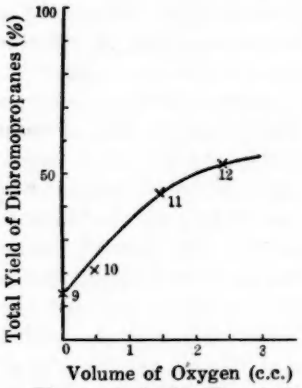

Fig. 2. Series IV (Exp. 9–12).

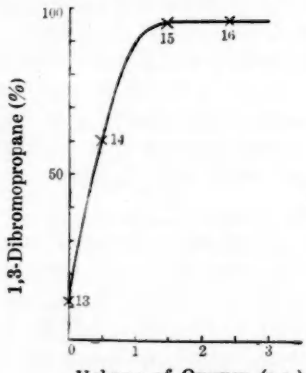

Fig. 3. Series V (Exp. 13–16).

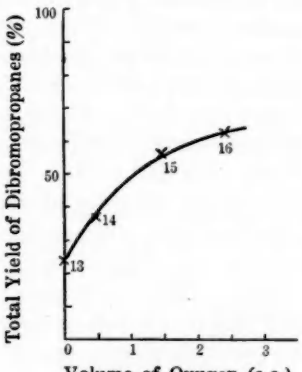

Fig. 4. Series V (Exp. 13–16).

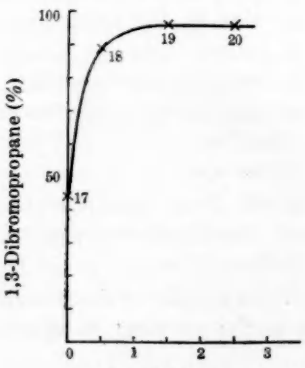

Fig. 5. Series VI (Exp. 17–20).

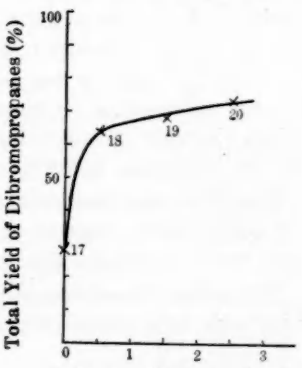

Fig. 6. Series VI (Exp. 17–20).

From Table 1 it can be seen that both the total yield of the product and the proportion of 1,3-dibromopropane in the product are greater in additions with peroxide-free allyl bromide in the presence of oxygen than in the additions with peroxide-containing allyl bromide in vacuum. On the one hand, part of oxygen introduced in gas into the reaction tube may be dissolved by the liquid and part of the dissolved oxygen may be transformed into a peroxide (one molecule from one). On the other hand, the peroxide may gradually decompose to liberate oxygen (one molecule from one) and part of the generated oxygen may leave the liquid. No matter how fast these changes may proceed, and no matter whether or not the changes from both sides go so far as to attain sooner or later the same equilibrium state, both the amount of peroxide alone and the total amount of the peroxide and molecular oxygen in the liquid where the addition takes place must be always greater in the experiments with peroxide-containing allyl bromide than in the experiments with peroxide-free allyl bromide. Such must be the case even if only one half of oxygen in the peroxide were liberated as molecular oxygen on decomposition, because then it could be much more naturally taken for granted that also one half of oxygen would be available in iodometry. In this connection it may be pointed out that neither oxygen nor peroxide oxidizes hydrogen bromide during the addition reaction with allyl bromide, but both do in the presence of platinum black.[2]

Under these circumstances the peroxide effect still appeared more marked in the additions with peroxide-free allyl bromide in the presence of oxygen. This observation permits to draw the following conclusions: (1) Molecular oxygen possesses catalytic activity in the sense of the so-called peroxide effect; and (2) the catalytic activity of the peroxide, if any, is smaller than that of molecular oxygen. It can not be decided, however, whether the peroxide is active at all or not. The fact that, while the action of oxygen is very regular as shown also by the experiments described below, the action of the peroxide is rather irregular as seen from Table 1, suggests the possibility that the peroxide exerts catalytic action not directly but through molecular oxygen generated by its decomposition. It must be taken into consideration that the peroxide is decomposed by hydrogen bromide rather quickly (exp. 4 and 7).

The above conclusions exclude the assignment of any catalytic effect to an undetectable amount of the peroxide and the effect observed with oxygen must be wholly due to the action of molecular oxygen.

Table 2 and the accompanying figures show the results of three series of additions with peroxide-free allyl bromide in the presence of various

volumes (0, 0.5, 1.5, and 2.5 c.c.) of oxygen. The capacities of the reaction tubes were 135–140 c.c. and the total volume of the reacting liquid (allyl bromide and hydrogen bromide) was 27 c.c. in condensed state. The experimental procedure was the same as described above, except that respective volumes of oxygen were admitted at sealing after evacuation. Purified allyl bromide was used in Series IV and V, and once distilled commercial product in Series VI. The time of reaction was 3 days in Series IV, and 5 days in Series V and VI. Additions to be related to one another were carried out as simultaneously as possible. For Series IV and V volumes of oxygen corrected to the normal temperature and pressure were used in the figures.

An experimental procedure as described above does not allow of taking an exact amount of hydrogen bromide nor of controlling the temperature at all. Moreover, the yield is calculated by weighing the dibromopropane mixture really obtained through routine processes for preparation involving the removal of unchanged allyl bromide with dimethylaniline. Hence, the numerical values of yields could not be expected to be exact nor even to be comparable with one another. Nevertheless, it can be seen that the yield increases with the amount of oxygen and with the time of reaction, and is greater in additions with impure allyl bromide than in additions with pure allyl bromide.

On the other hand, it is possible to make more exact mention of the relation between the amount of oxygen and the composition of the product. When the amount of oxygen is 1.5 c.c. and more, the proportion of 1,3-dibromopropane in the product is constant at about 95%, irrespective of the time of reaction and the purity of allyl bromide. In exp. 2 where once distilled allyl bromide was used as in exp. 17–20, and oxygen as much as 4.8 c.c. was admitted, the proportion of 1,3-dibromopropane was 95% (see Fig. 2). Also in the range of less than 1.5 c.c. of oxygen the three series are qualitatively similar: the proportion of 1,3-dibromopropane increases rapidly with the increase of oxygen. In this region, however, the formation of 1,3-dibromopropane is favoured slightly by the longer time of reaction and greatly by the presence of impurities. It is worthy of note that, although the yields of exp. 5 and 8 carried out with purified allyl bromide deviate from the curve of Fig. 2, the proportions of 1,3-dibromopropane come well into line with the results of Series IV (Fig. 1).

Exp. 2 falls in the region where impurities do not affect the composition of the product, which justifies the comparison of it with exp. 1. Allyl bromide was purer in exp. 5 than in exp. 3, and, therefore, a comparison as made above is reasonable. Exp. 6, 7, and 8 were carried out

with portions from the same purified specimen, and they are quite comparable.

As mentioned above, impurities in allyl bromide influence the catalytic action of oxygen, exaggerating both the inversing effect on the direction of addition and the increasing effect on the yield of the product. But there has been no indications to the possibility that impurities may play the leading part in the so-called peroxide effect.

In this way the action of oxygen has been established. The next problem is to decide whether the catalytic action of oxygen is homogeneous (dissolved oxygen acting) or heterogeneous (oxygen adsorbed on the glass wall coming into play). Experiments devised for the solution of this problem are now under way.

In conclusion the authors express their hearty thanks to the Imperial Academy of Japan for a grant.

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